ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF BLOCK COPOLYMERS VIA COMBINATION OF CATIONIC RING OPENING AND ATOM TRANSFER RADICAL POLYMERIZATIONS

M.Sc. Thesis by

Nadin NARSİSOĞLU

Department : Polymer Science and Technology

Programme: Polymer Science and Technology

JANUARY 2004

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KATYONİK HALKA AÇILMASI VE ATOM TRANSFER RADİKAL POLİMERİZASYON YÖNTEMLERİ İLE DİBLOK KOPOLİMERLERİN SENTEZİ

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LIST OF ABBREVIATIONS

M_n **:** Number average molecular weight of polymer

M_w **:** Weight average molecular weight of polymer

PMMA **:** Poly(methyl methacrylate)

PSt **:** Polystyrene

PEtOZO **:** Poly(2-ethyl-2-oxazoline)

P(MMA-*b*-EtOZO) **:** Poly(methyl methacrylate-*b*-2-ethyl-2-oxazoline)

P(St-*b*-EtOZO) **:** Poly(styrene-*b*-2-ethyl-2-oxazoline)

I, M **:** Initiator and monomer respectively

PMDETA **:** *N*,*N*,*N*$^{'}$,*N*$^{''}$,*N*$^{''}$-(pentamethyldiethylenetriamine)

DIP **:** Double Isomerization Polymerization

AB **:** Allyl Bromide

BPE **:**1-Bromo-1-phenyl ethane

EIBR **:** Ethyl-2-bromo isobutyrate

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LIST OF SYMBOLS

$\mathbf{M_n}$	**:** Number average molecular weight of polymer
$\mathbf{M_w}$	**:** Weight average molecular weight of polymer
$\mathbf{k_a}$, $\mathbf{k_d}$	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
$\mathbf{k_i}$, $\mathbf{k_p}$, $\mathbf{k_t}$	**:** Rate constants of initiation, propagation and termination steps in radical polymerization

SYNTHESIS OF BLOCK COPOLYMERS VIA COMBINATION OF CATIONIC RING OPENING AND ATOM TRANSFER RADICAL POLYMERIZATIONS

SUMMARY

2-oxazolines are five-membered cyclic imino ethers which are known to polymerize via cationic ring opening polymerization (CROP) to produce poly(N-acylethylenimine)s. The polymerization occurs through a 'living' form and the product polymers become hydrophilic or hydrophobic, depending on the nature of the acyl group. 2-oxazolines are useful compounds for the architectural control of polymeric material. Various applications of oxazoline polymers are based on the structures of block and graft copolymers.

The synthesis of block copolymers is obviously one of the polymer synthesis areas where living polymerization techniques are most effective and convenient. Among these techniques atom transfer radical polymerization (ATRP) is effective for the controlled molecular weight and chain end functionality. Block copolymers may be synthesized via reactions of end-functionalized polymers, where macroinitiators with terminal functions that can initiate the polymerization of a second monomer, are used.

In this study, amphiphilic diblock copolymers consisting of methyl methacrylate (MMA) and 2-ethyl-2-oxazoline (EtOZO) were synthesized via combination of atom transfer radical polymerization and cationic ring opening polymerization. Poly(methyl methacrylate) and polystyrene macroinitiators were synthesized by ATRP, and used in the cationic ring opening polymerization of 2-ethyl-2-oxazoline to produce poly(methyl methacrylate-*b*-2-ethyl-2-oxazoline) (P(MMA-*b*-EtOZO)) and poly(styrene-*b*-2-ethyl-2-oxazoline) (P(St-*b*-EtOZO)) block copolymers.

KATYONİK HALKA AÇILMASI VE ATOM TRANSFER RADİKAL POLİMERİZASYON YÖNTEMLERİ İLE BLOK KOPOLİMER SENTEZİ

ÖZET

2-Okzazolinler katyonik halka açılması metodu ile polimerleşerek poli(N-açiletilenimin)leri oluşturan siklik imino eterlerdir. Okzazolin polimerizasyonu, 'yaşayan' karakterlidir ve oluşan polimerler açil gruplarının yapısına bağlı olarak hidrofilik veya hidrofobik özellik gösterir. 2-Okzazolinler, polimerik materyallerin mimari yapılarının kontrolü için yararlı bileşiklerdir. Okzazolin polimerlerinin çeşitli uygulamaları blok ve graft kopolimerlerinin sentezine dayanır.

Yaşayan polimerizasyon tekniklerinin en etkili ve uyumlu olduğu polimer sentez alanlarından birisi blok kopolimer sentezidir. Bu teknikler içinde en etkili olanı, elde edilen polimerlerin molekül ağırlığı ve uç grup kontrolünün sağlandığı atom transfer radikal polimerizasyonudur (ATRP). Blok kopolimerler uç grup fonksiyonlu polimerlerin reaksiyonları ile sentezlenebilir. Bu yöntemde ikinci bir monomerin polimerizasyonunu gerçekleştirebilen uç grup fonksiyonalitesine sahip makrobaşlatıcılar kullanılır.

Bu çalışmada metil metakrilat (MMA) ve 2-etil-2-okzazolin (EtOZO) zincirlerinden oluşan amfifilik diblok kopolimerler, atom transfer radikal polimerizasyon ve katyonik halka açılması polimerizasyon tekniklerinin birlikte kullanılmasıyla sentezlenmiştir. Poli(metil metakrilat) (PMMA) ve polistiren (PSt) makrobaşlatıcıları ATRP ile sentezlenmiş ve 2-etil-2-okzazolin monomerinin katyonik halka açılması polimerizasyonunda kullanılmıştır. Bu yolla poli(metil metakrilat-*b*-2-etil-2-okzazolin) (P(MMA-*b*-EtOZO)) ve poli(stiren-*b*-2-etil-2-okzazolin) (P(St-*b*-EtOZO)) blok kopolimerleri sentezlenmiştir.

1. INTRODUCTION

The polymerization of heterocyclic 2-substituted 2-oxazolines (endo-imino ethers) has been studied in depth by several research groups since the 1960s [1-3]. These monomers are known to be polymerized through cationic ring opening polymerization producing poly(N-acylethyleneimine)s. Because of their ease of preparation, the resulting polyoxazolines have found wide interest in medicine and technology. In particular their low toxicity (LD50>4g/kg) [4] and high hydrophilicity have speeded up possible applications as drug-delivery systems, hydrophilization of surfaces, and slow delivery vehicles.

In general, the polymerization reaction follows a living mechanism leading to well-defined degrees of polymerization and low polydispersities [3] which exhibit variable amphiphilicity. Depending on the kind of 2-substituent group on the oxazoline ring, it is possible to obtain hydrophilic or hydrophobic polymers. With methyl or ethyl groups hydrophilic and water soluble polymers are obtained, whereas with longer alkyl substituents or aromatic substituents hydrophobic polymers can be synthesized.

The polymerization of 2-substiuted 2-oxazolines occurs without chain transfer reactions or terminating reactions under appropriate conditions. Therefore it is very attractive for the elaboration of different macromolecular architectures like block and graft copolymers and non ionic hydrogels [5-7].

The synthesis of block copolymers is obviously one of the polymer synthesis areas where living polymerization techniques are most effective and convenient. Among these techniques atom transfer radical polymerization(ATRP) is effective for the controlled molecular weight and chain end functionality. Block copolymers may be synthesised via reactions of end-functionalized polymers, where macroinitiators with terminal functions that can initiate the polymerization of a second monomer, are used.

In the present study, the synthesis of amphiphilic block copolymers via the cationic ring opening polymerization of 2-ethyl 2-oxazoline is described using macroinitiators. Halogen ended macroinitiators PMMA and PSt are obtained by ATRP and used in the polymerization of 2-ethyl-2-oxazoline which can be initiated by allyl halides [8].

2. THEORETICAL PART

2.1. Controlled/‘Living’ Radical Polymerization

The term controlled/ ‘living’ polymerization (C/LRP) was initially used to describe a chain polymerization in which chain breaking reactions were absent [9,10]. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. However, transfer and termination often occur in real system. Thus, living polymerization (no chain breaking reactions) and controlled polymerization (formation of well defined polymers) are two separate terms.

A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality.

Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected. On the other hand, living polymerizations will lead to well defined polymers only if the following additional presquisites fullfilled:

-initiation is fast in comparison with propagation
-exchange between species of different reactivities is fast in comparison with propagation
-the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

Well defined polymers may be formed in radical polymerization only if chains are relatively short and concentration of free radicals is low enough. There is apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals. The controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weight sufficiently low. This

necessitates a relatively high concentration of the initiator, or in other words, low $[M]_0 / [I]_0$ ratios. However, when $[I]_0$ is high, since the termination is bimolecular, contribution of termination becomes more significant when a large concentration of radicals [P**.**] is generated.

Therefore establishing an exchange between dormant and active species is necessary to solve this discrepancy. The concentration of dormant species can be equal to $[I]_0$, and the concentration of momentarily growing species to [P**.**]. The total number of growing chains will be equal to $[I]_0$, and radicals would be present at a very low stationary concentration, [P**.**], and therefore the contribution of termination should be very low.

The three approaches have been used to control radical systems. The best examples of the first approach include stable free radical polymerization (SFRP), atomic transfer radical polymerization (ATRP), and photolabile iniferters. The second approach is less common and may be included some organometallic species such as $Cr^{(III)}$ or Al derivatives as well as nonpolymerizable alkenes such as stilbene or tetrathiafulvalene. The last approach can be best exemplified chemistry, via methacrylate monomers [11,12].

2.1.1 Atom Transfer Radical Polymerization (ATRP)

The name of atom transfer radical polymerization (ATRP) comes from the atom transfer step, which is the key elemantary reaction responsible for the uniform growth of the polymeric chains. ATRP is one of the most widely used living free radical polymerization techniques and seems to be the most versatile one. This technique can successfully be applied to the living radical polymerization of methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [13-16].

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. For a successful ATRP, other factors, such as solvent, temperature, concentrations and solubility of all components, and sometimes the order of their addition must be also taken into consideration.

The general mechanism of ATRP which is schematically represented in (2.1), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^1, in a redox process [17]. Upon halogen abstraction, the free radical formed (the active species) can undergo propagation. However, the free-radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of free radicals is quite low, resulting in a reduced amount of irreversible radical-radical termination . The final result is that degrees of polymerization (DP) can be predetermined ($DP=\Delta[M]/[I_o]$) and M_w/M_n is quitelow(1,05-1,5), and good control of functionalities is achieved [18].

Initiation

$$R\text{-}X + Cu(I)/Ligand \underset{k^o_d}{\overset{k^o_a}{\rightleftharpoons}} R\cdot + XCu(II)/Ligand \qquad (2.1)$$

$$R\cdot \xrightarrow{k_i} + M$$

$$R\text{-}M\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M\cdot + XCu(II)/Ligand$$

$$R\text{-}M\cdot \xrightarrow{k_p} + M_n$$

Propagation

$$R\text{-}M_n\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M_n\cdot + XCu(II)/Ligand$$

Termination

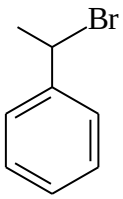
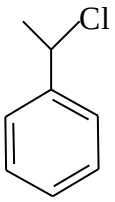
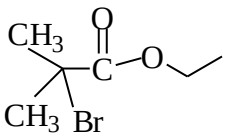
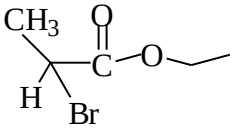
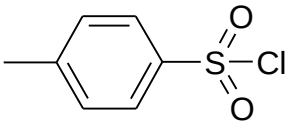
$$R\text{-}M_n\cdot + R\text{-}M_m\cdot \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R + R\text{-}M_nH / R\text{-}M_m^{=}$$

2.1.1.1 Initiators

There is a large class of halogenated compounds that can be used as initiators in ATRP. The only requirement is that the initiator must have labile halogen attached to an atom containing radical stabilizing substituents [19].

In ATRP both effective initiation and good control of the polymerization rely heavily on the position of the equilibrium in both the initiation and the propagation steps, and also on reactivities of the radicals generated in the initiation step. Thus, choosing a suitable organic halide and $Cu^{(I)}$ halide is necessary for the controlled polymerization. The most frequently used initiator types in ATRP systems are given in Table 2.1.

Table 2.1 Types of initiators used in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methylmethacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

2.1.1.2 Monomers

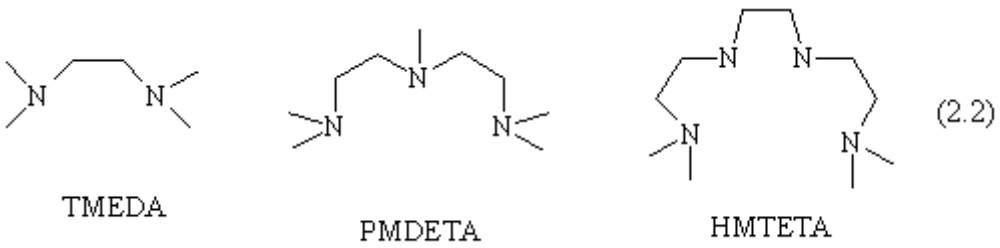
Styrenes, acrylates, methacrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and dienes can be polymerized by ATRP, and well defined polymers are achieved.

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally,since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

2.1.1.3 Ligands

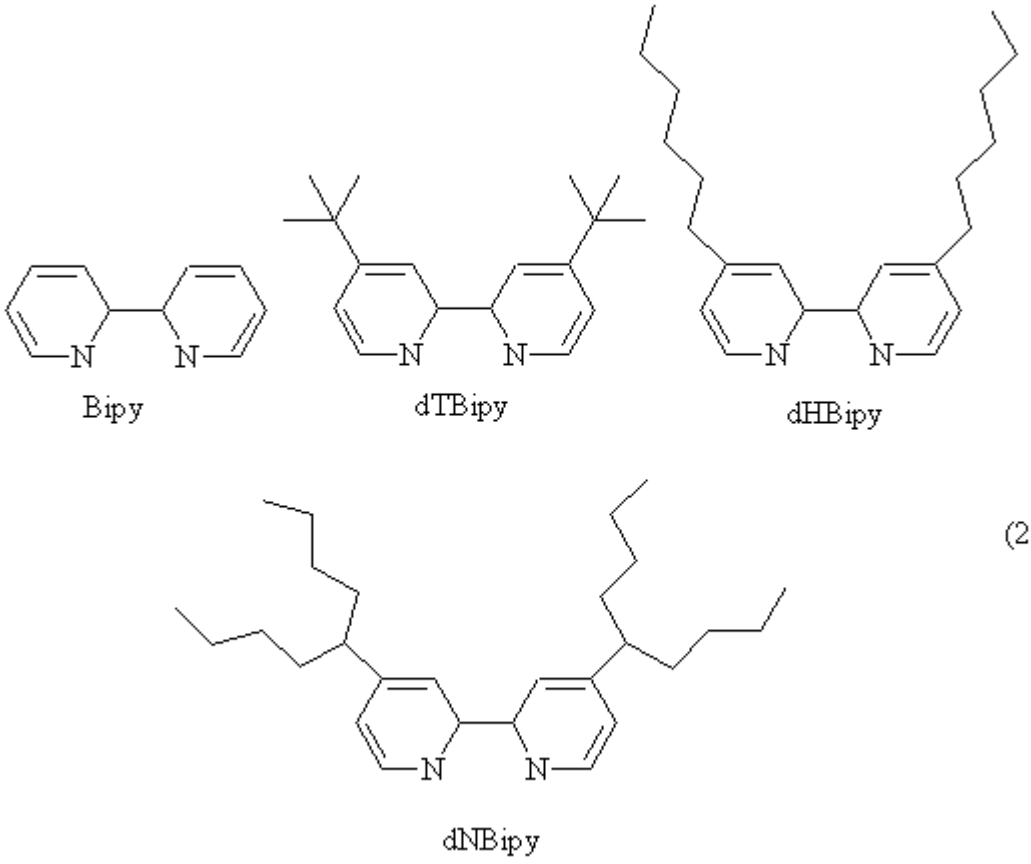
The main role of ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as *N,N,N',N'',N''* pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris [2-(dimetylamino) ethyl]amine (Me-TREN) and alkylpyrdylmethanimines are also used.

Nitrogen based ligands:



(2.2)

Derivatives of 2,2-bipyridine:



(2.3)

2.1.1.4 Transition Complexes

The most important component of ATRP is the catalyst. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron, Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be upon oxidation to accommodate a halogen. Fourth, the ligand should complex the metal relatively strongly. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$ / $Al(OiPr)_3$.

2.1.1.5 Solvents

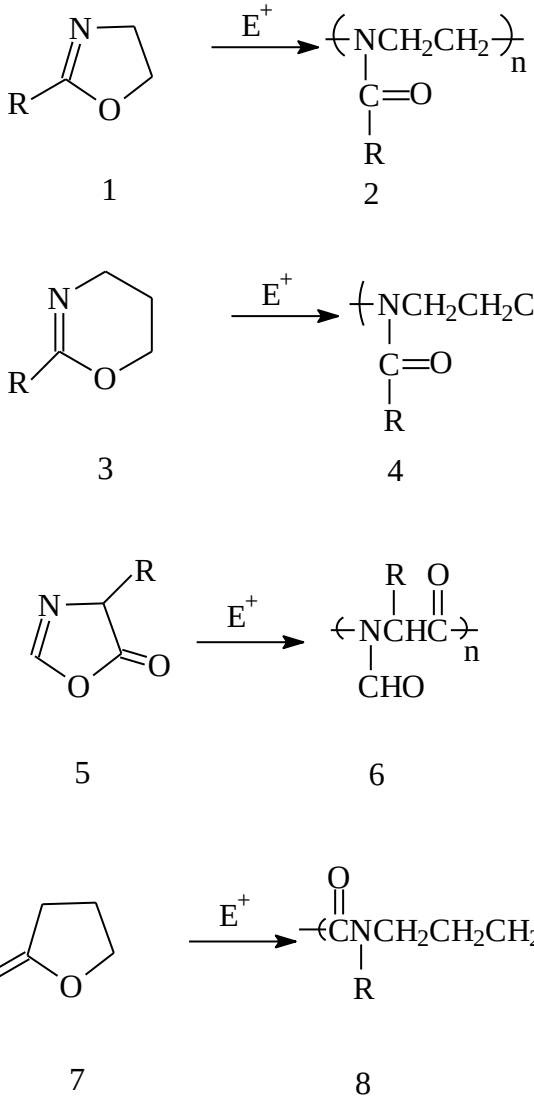
ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethylformamide (DMF), ethylene

carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of diffferent monomers.

2.2 Cationic Ring Opening Polymerization Of Cyclic Imino Ethers

Cyclic imino ethers are compounds containing the –N=C-O- group in the endocyclic and exocyclic structures. The characteristic feature of the polymerizatioon of this group of monomers is that isomerization occurs during the propagation step, thus the structure of the repeating unit is not directly related to the structure of the ring as in other ring-opening polymerizations.

Cyclic imino ethers of five to seven membered systems possess polymerizability through ring opening mechanisms as seen in (2.4).

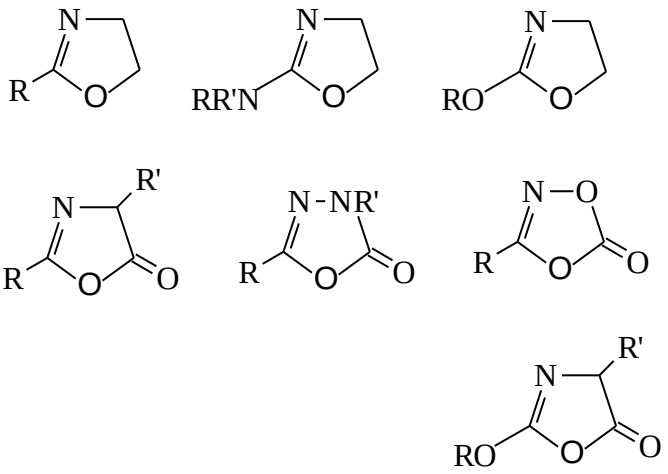
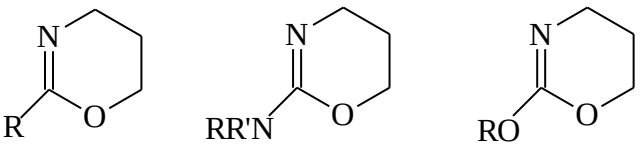
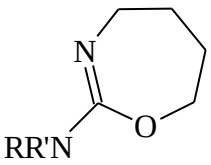


(2.4)

2-substituted 2-oxazolines (ROZOs; 1) give poly (N-acylethylenimine)s (PROZOs; 2) via ring opening izomerization polymerization. Cationic initiators induce the ring-opening polymerization of 5,6-dihydro-4H-1,3-oxazines(3; 6-membered cyclic imino ethers) to give poly(N-acyltrimethylenimine)s (4) [20]. 2-Unsubstituted 5-oxazolones (5) polymerize with a cationic initiator to produce poly(N-formyl-α-peptide)s (6) [21].The polymerization of cyclic exo imino ethers , 2-iminotetrahydrofuranes (7), proceeds in the presence of various cationic initiators, yielding polyamides (8) [22].
Cyclic imino ethers can be classified into two categories; cyclic endo- and cyclic exo-imino compounds, as summerized in Table 2.2.

Numerous cationic initiators have been used for the polymerization of cyclic imino ethers [2,23,24] . Lewis acids, stable cationic salts, strong protonic acids and their salts, ester of sulfuric sulfonic and picric acids and acid anhydrides, and alkyl halides, are typical initiators and are listed in table 2.3.

Table 2.2 Types of cyclic imino ether monomers

Ring size	Cyclic *endo*-imino ethers
Five-membered ring	
Six-membered ring	
Seven-membered ring	

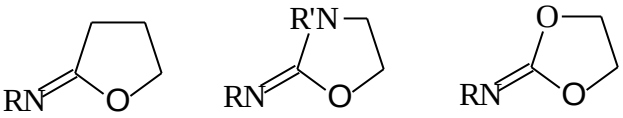
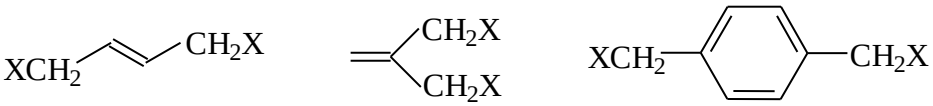
Ring size	Cyclic *exo*-imino ethers
Five-membered ring	

Table2.3 Types of initiators for the polymerization of cyclic imino ethers

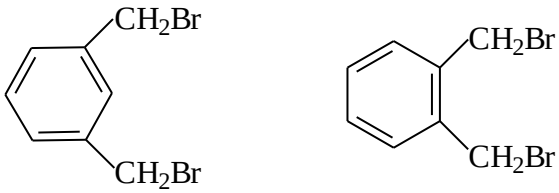
Type of initiator	Example	Type of initiator	Example
Sulfonate esters	p-$MeC_6H_4SO_3Me$	Lewis acids	BF_3
	p-$O_2NC_6H_4SO_3Me$		$AlCl_3$
	CF_3SO_3Me		$TiCl_4$
	FSO_3Me		PF_5
Sulfate esters	$(MeO)_2SO_2$		SbF_5
Sulfonic anhydrides	$(MeSO_2)_2O$	salts of Lewis acids	$Et_3O^+BF_4^-$
alkyl haloformates	MeOCOCl		
Alkyl halides	$PhCH_2Cl$		
	$PhCH_2Br$	oxazolinium salts	
	MeI	electron acceptors	$(NC)_2C=C(CN)_2$
Protonic acids	$HClO_4$		7,7,8,8- tetracyano-quinodimethan
	CF_3SO_3H		
	H_2SO_4		
	HBr		

Allyl-type dihalides, i.e. 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-1-propene, were employed as bifunctional initiators.The degree of polymerization (DP) values of the polymers agreed well with the feed ratios of the monomer to initiator. A kinetic study revealed that the polymerization of 2-methyl-2-oxazoline using these bifunctional initiators is a ‘fast-initiation-slow propagation system’. As a bifunctional initiator, xylylene diiodide and dibrimide are also useful. Star-shaped oxazoline polymer was obtained with an allylic tetrahalide initiator, tetrakis(bromomethyl)-ethylene [25,26]. Some examples of allyl type difunctioanal initiators are given in (2.5)



X = Br, Cl X = I, Cl X = I, Br, Cl

(2.5)



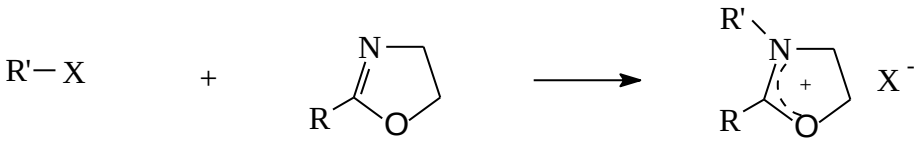
2.2.1 Polymerization of 2-Oxazolines

The ring-opening polymerization of 2-oxazolines was first reported by Kayiga et al. in 1966 [27]. Except for the case of Double Isomerization Polymerization (DIP) of 2-amino-2-oxazolines, 2-oxazolines are polymerized to produce the corresponding derivatives of poly (N-acylethylenimine)s (2) via ring-opening isomerization.

Detailed kinetic studies on the polymerizations of 1 and 3 have shown that the polymerizations proceeds via two different types of propagating species, ionic and covalent, depending on the ring size, monomer substituent, and nature of the initiator [28-30]. General mechanism for initiation and propagation of 2-oxazolines are shown in (2.6) for ionic type, and in (2.7) for covalent type.

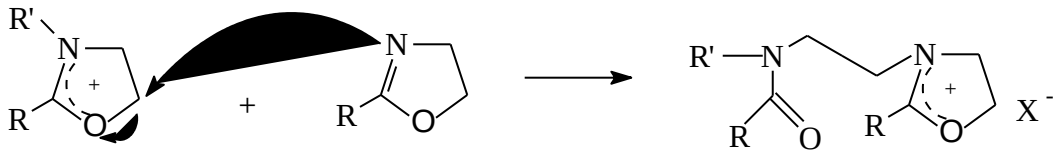
Ionic Type

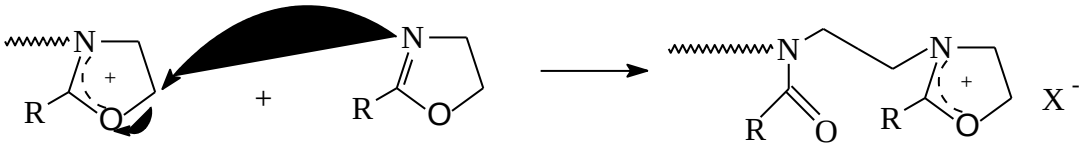
Initiation



(2.6)

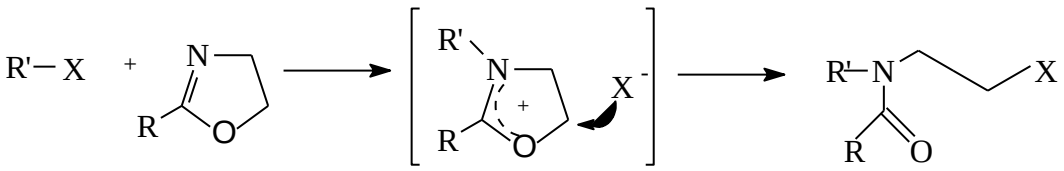
Propagation





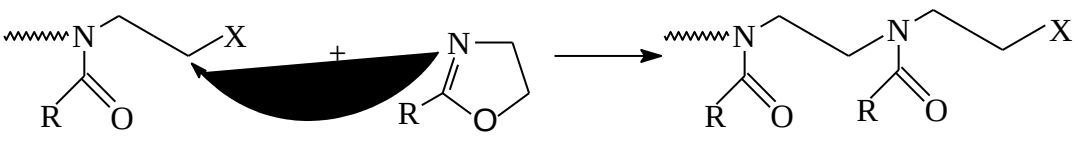
Covalent Type

Initiation

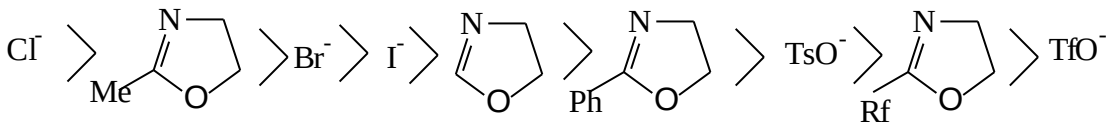


Propagation

(2.7)



Growing species in the polymerization of several 2-oxazolines have been examined with benzyl chloride, with methyl iodide, with MeOTs, and with MeOTf as initiators. The results are summarized in Table 2.4, together with the case of DIP of 2-amino-2-oxazolines.The monomers and counteranions are placed by considering the order of nucleophilicities. Concerning the nature of propagating species in the polymerization of 2-oxazolines, the above monomers and counteranions are arranged in the following order of nucleophilicity shown in (2.8), where the concentration is not considered.

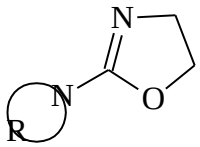
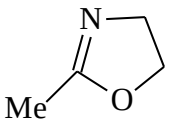
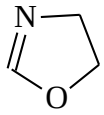
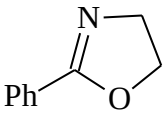
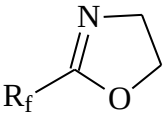


(2.8)

Ionic and covalent polymerization mechanisms are explained by the balance of nuchleophilicities between monomers and counteranions. DIP of 2-amino-2-oxazolines is out of this relationship; since the propagation involves additional isomerization mechanisms.

For example, the polymerization of unsubstituted 2-oxazoline (9) with an initiator of methyl tosylate propagates via an ionic species of oxazolinium tosylate .The kinetics obeys a bimolecular S_N2-type reaction between an ionic intermediate and monomer. However, the polymerization with methyl iodide as an initiator proceeds via a covalently bonded species possessing electrophilic reactivity. In this case, the ring of the generated oxazolinium salt is rapidly opened by the attack of the iodide counteranion. For 2-methyl-2-oxazoline, the polymerization proceeds via the ionic propagating species with iodide, tosylate,and triflate counteranion, whereas the covalent propagating species can be observed with benzyl chloride as an initiator.

Table 2.4 Types of propagating species in the polymerization of 2-oxazolines

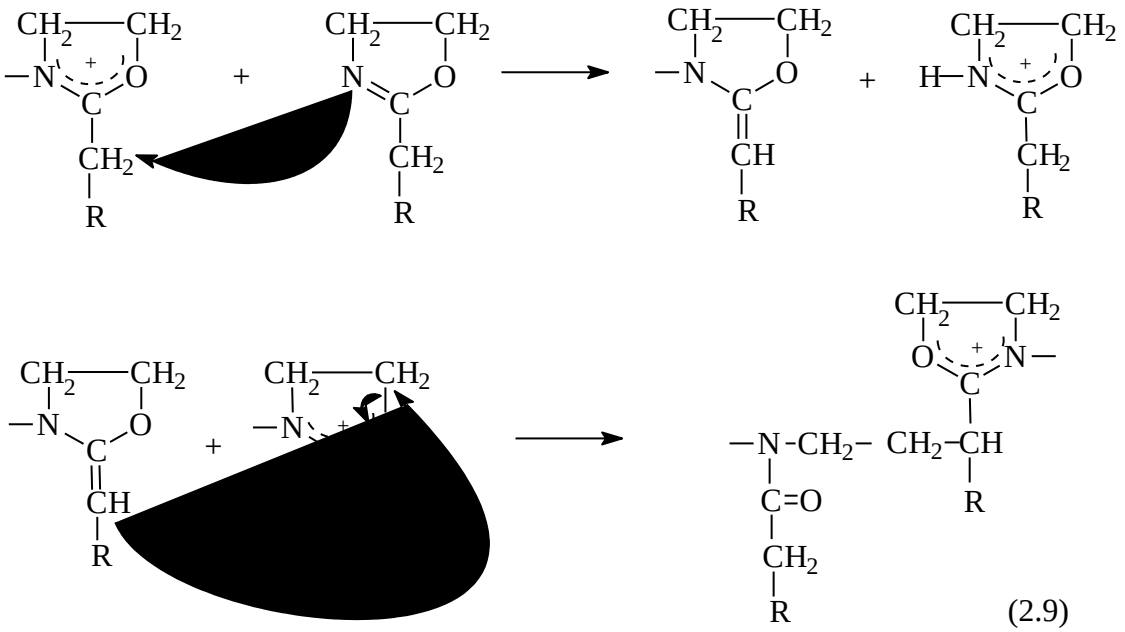
Monomers / References	Counteranions, X^-				
	Nucleophilicity ←				
	Cl	I	TsO	TfO	
	ionic and covalent (DIP)	ionic and covalent (DIP)	ionic	ionic	31,32
	covalent	ionic	ionic	ionic	33,34
	covalent	covalent	ionic	ionic	35
	-	covalent	ionic	ionic	36
	-	covalent	covalent	ionic	37,38

Nucleophilicity ↑

$R_f = C_2F_5, C_3F_7$

The introduction of the strong electron-drawing perfluoroalkyl group at the 2-position of 1 dramatically reduces the nucleophilicity; the covalent propagating species can be extensively seen even with methyl tosylate as an initiator in the polymerization of 2-perfluoroalkyl-2-oxazoline.

Polymerization of oxazolines is the rare example of cationic ring opening polymerization in which chain transfer to polymer is of no importance for the whole group of monomers. This is because the imino group of the monomer is converted upon propagation into an amide group having much lower nucleophilicity. Thus, the cationic polymerization of oxazolines is believed to be of living type, although at least one side reaction affecting the living character has been identified in the polymerization of oxazolines having $–CH_2-$ group in the substituent (2.9) [39].

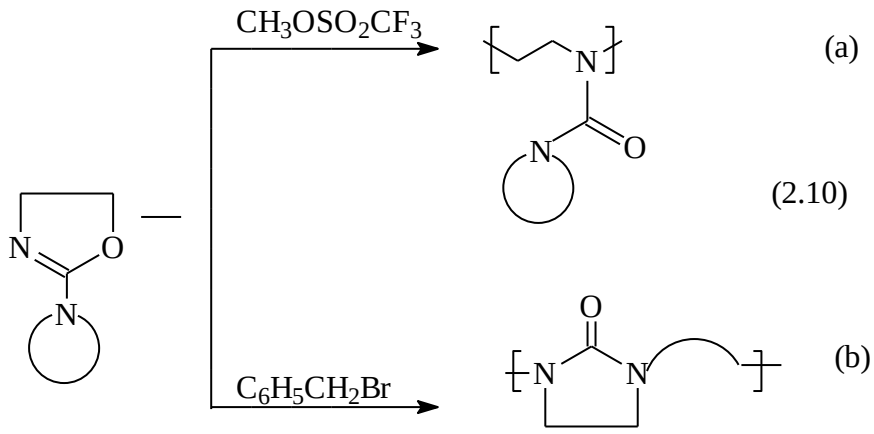


(2.9)

2.2.2 Double Isomerization Polymerization(DIP)

Another mode of polymerization for 2-oxazolines was revealed with the polymerization studies of 2-oxazolines having cyclic amine substituents at the 2-position [31,32,40-42]. It is presented under the name of Double Isomerization Polymerization(DIP), meaning 'isomerization polymerization accompanying the isomerization of the growing species'.

Oxazoline substituted at 2-position with cyclic imino group may, depending on the kind of initiator used, undergo conventional polymerization giving structure (a) or may undergo double isomerization polymerization. In the latter process, the isomerization of propagating species occurs: the 2-oxazoline ring rearranges to a 5-membered cyclic urea unit and the cyclic imine moiety undergoes ring opening, leading to repeating unit (b) as shown in (2.10).



(a)

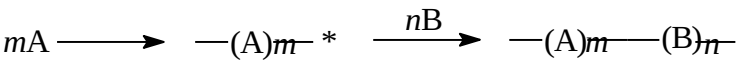
(2.10)

(b)

2.3 Block Copolymers

The synthesis of block copolymers is obviously one of the polymer synthesis areas where living polymerization is most effective and convenient. In general , block copolymers may be synthesised either via sequential living polymerization or via reactions of end- functionalized polymers that include living polymers.

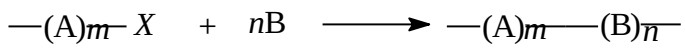
2.3.1 Sequential Living Cationic Polymerization



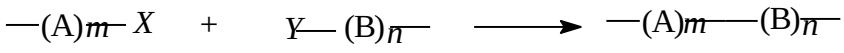
(2.11)

The sequential living polymerizatian (2.11) of two monomers is perhaps the most straightforward method to synthesize block copolymers, and sometimes the successful formation of block copolymers by this way is taken as evidence for the occurance of living polymerization. Namely ,monomer A is polymerized into a living cationic polymer, from the living end of which another monomer B is polymerized again in a living fashion into an AB-block copolymer. Thus the synthesis can be carried out simply in a one pot, but the propagation mechanisms for the two monomers should accordingly be the same, which sometimes limits the range of monomer (segment) cominations.

2.3.2 Reactions of End-Functionalized Polymers



(2.12)



(2.13)

The reactions of end-functionalized polymers may be divided into two subclasses, the living polymerization from macroinitiators (2.12) and the polymer coupling reactions (2.13). The former uses end-functionalized polymers with a terminal function(*X*) that can initiate the living polymerization of a second monomer. The latter involves two end-functionalized polymers, where the terminal functions , X and Y, react with each other to combine them into a block copolymer.

3.EXPERIMENTAL PART

3.1 Chemicals Used

a) Monomers

Methyl methacrylate (MMA, 99% Aldrich) was passed through basic alumina column to remove inhibitors and then was vacuum-distilled over CaH_2 before use. Styrene (St, 99% Aldrich) was passed through basic alumina column to remove inhibitors and then was vacuum-distilled over CaH_2 before use. 2-ethyl-2-oxazoline (EtOZO, 99% Aldrich) was stirred over CaH_2 and distilled under nitrogen.

b) Solvents

Acetonitrile (AN, 99% Merck) was distilled over CaH_2. Tetrahydrofuran (THF, 99.8%, J.T.Baker HPLC grade) was dried and distilled over lithium aluminium hydride.

c) Other Chemicals

Sodium iodide was dried under vacuum at 100^{o}C for at least 4 hours prior to use. Unless otherwise specified, other reagents were purchased from commercial sources and used as received.

3.2 Synthesis of Poly(2-ethyl-2-oxazoline) (PEtOZO) by Cationic Ring Opening Polymerization

Into a tube equipped with a magnetic stirring bar and a rubber septum was connected to a vacuum line. The tube was dried by heating under vacuum. After cooling to room temperature, an argon inlet was introduced then the initiator,solvent, and monomer were added in the order mentioned. Vacuum-argon was applied several times to the reaction medium. The flask was disconnected under argon and was placed into a thermostatically controlled bath at 80^{o}C. After a given time the tube was cooled to room temperature and methanolic potassium hydroxide was introduced into the reaction tube in order to terminate the polymerization and introduce

hydroxyl groups at the end of the polymer chains. Then the reaction mixture was poured into diethyl ether. The precipitated polymer was filtered and dried under vacuum at 50^{o}C. Conversions were determined gravimetrically.

P(EtOZO)s were prepared in acetonitrile at 80^{o}C using allyl bromide, 1-bromo-1-phenyl ethane, and ethyl-2-bromo isobutyrate as initiators.

3.3 Synthesis of Poly(methyl methacrylate) (PMMA) and Polystyrene (PSt) by ATRP

General procedure for the atom transfer radical polymerization was as follows: Into a schlenk tube eqipped with a magnetic stirring bar, monomer, solvent, ligand, catalyst and initiator were added in the order mentioned. The tube was degassed by three freeze-thaw cycles, left under vacuum and placed in a thermostated oil bath at 90^{o}C for PMMA and at 110^{o}C for PSt. After a given time polymerization was terminated by cooling the tube to room temperature. The reaction mixture was diluted with THF and passed through a column of neutral alumina to remove metal salt. THF was passed through the column of neutral alumina right before the reaction mixture was passed, in order to prevent the polymer to be kept inside the column. The excess of THF and unreacted monomer was evaporated under reduced pressure. PMMA was dissolved in THF and precipitated in methanol and filtered twice and dried under vacuum. Conversions were determined gravimetrically. PMMA was prepared in 50 vol % diphenylether (DPE) solution at 90^{o}C using CuCl / *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalyst and ethyl-2-bromo isobutyrate as the initiator.

PSt, was prepared in bulk at 110^{o}C using CuBr as the catalyst, PMDETA as the ligand and 1-bromo-1-phenyl ethane as the initiator.

3.4 Synthesis of Poly(styrene-b-2-ethyl-2oxazoline), (P(St-b-EtOZO), and Poly(methyl methacrylate-b-2-ethyl-2-oxazoline) by Cationic Ring Opening Polymerization

Into a tube equipped with a magnetic stirring bar and a rubber septum was connected to a vacuum line. The tube was dried by heating under vacuum. After cooling to room temperature, an argon inlet was introduced then macroinitiator, monomer and

solvent, were added in the order mentioned. While using PMMA macroinitiator NaI was added into rection mixture. Vacuum-argon was applied several times to the reaction medium. The flask was disconnected under argon and was placed into a thermostatically controlled bath at 110^{o}C. After a given time the tube was cooled to room temperature and methanolic potassium hydroxide was introduced into the reaction tube in order to terminate the polymerization and introduce hydroxyl groups at the end of the polymer chains. Then the reaction mixture was poured into diethyl ether. Polymer The precipitated polymer was filtered and dried under vacuum at 50^{o}C. Conversions were determined gravimetrically.

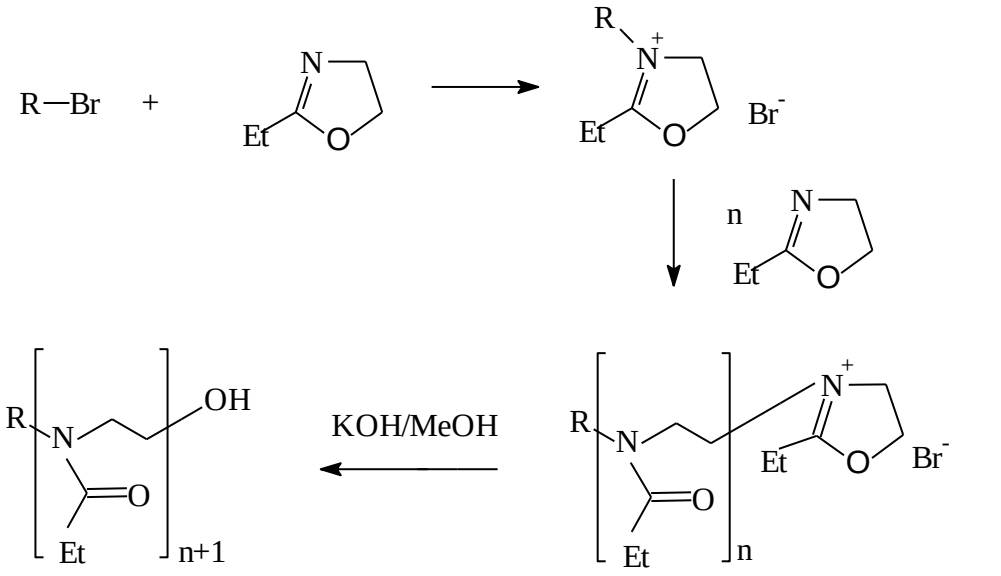
3.5 Characterization

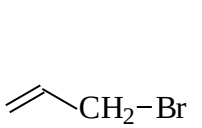
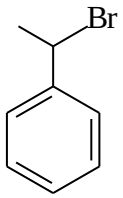
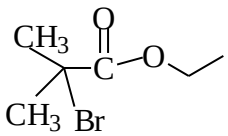
Gel permeation chromaographic (GPC) analysis were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as the eluent at a flow rate of 0,3 mL/min. Molecular weight of the polymers was calculated with the aid of polystyrene standarts. ^{1}H-NMR spectra was recorded on a Bruker AC 250 (250 MHz for proton and 62.90 MHz for carbon) in $CDCL_3$.

4.RESULTS AND DISCUSSIONS

4.1 Synthesis of PEtOZO Homopolymers

Allyl bromide(1), 1-bromo-1-phenyl ethane(2) and ethyl 2-bromo-isobutyrate(3) was used to initiate the cationic ring opening polymerization of 2-ethyl-2-oxazoline at 80^{o}C. The representation of the synthesis is seen in Scheme 4.1. 1-Bromo-1-phenyl ethane was used as a model initiator for PSt, and ethyl-2-bromo isobutyrate was used for PMMA macroinitiators.



Where R-Br is  (1),  (2),  (3)

Scheme 4.1 Synthesis of PEtOZO homopolymers

GPC analysis were done for each of the PEtOZO homopolymers. Theoretical molecular weights were calculated. The results are presented in Table 4.1 . The GPC trace of PEtOZO homopolymer (P-II) is given in figure 4.1.

Table 4.1 Synthesis of PEtOZO homopolymers

Run	Monomer	Init.	Time (h.)	Conv. (%)	Mn_{theo}[b]	Mn_{GPC}[c]	M_w/M_n
P-I[a]	EtOZO	AB	19	96	7600	6200	1,12
P-II[a]	EtOZO	BPE	23	99	7900	4000	1,6
P-III[a]	EtOZO	EIBR	30	99	7900	5600	1,9

AB: Allyl Bromide

BPE: 1-bromo-1-phenyl ethane

EIBR: Ethyl-2-bromo isobutyrate

[a] $[M]_0/[I]_0$: 80, the polymerization was carried out at 80^0C, in acetonitrile(AN) (EtOZO/AN= 1, v/v), $[M]_0$mol l^{-1} = 9,9

[b] $M_{n\ (theoretical)} = ([M]_0/[I]_0)$ x (conversion %) x $MW_{monomer}$

[c] Molecular weights were calculated by the aid of polystyrene standarts.

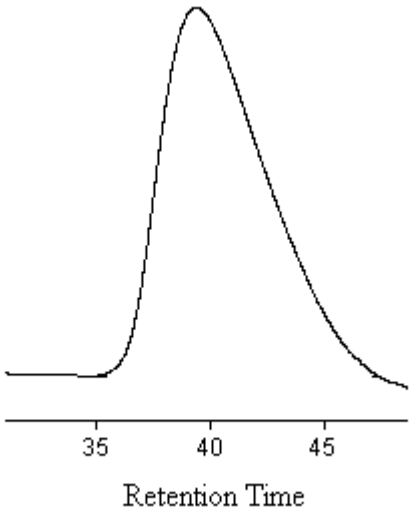
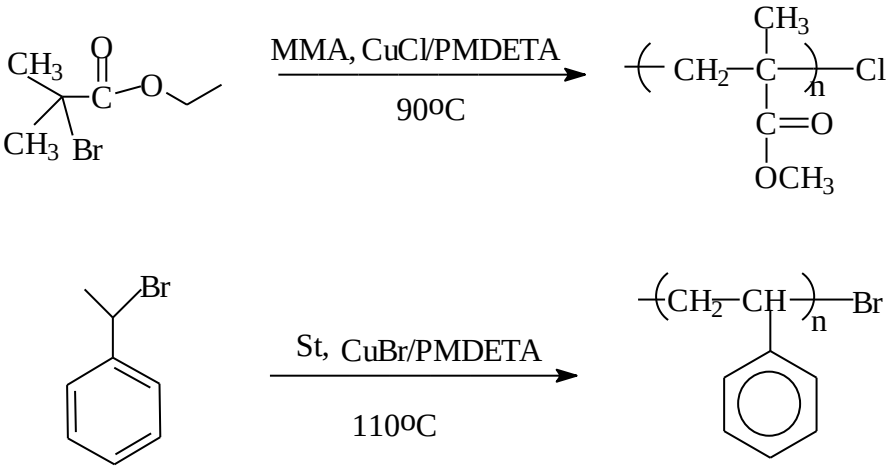


Figure 4.1 GPC trace of PEtOZO homopolymer (P-II)

4.2 Synthesis of PMMA and PSt Macroinitiators by ATRP

Ethyl-2-bromo isobutyrate and 1-bromo-1-phenyl ethane was used to initiate the controlled polymerization of PMMA, and PSt. The representation of the synthesis is seen in Scheme 4.2.

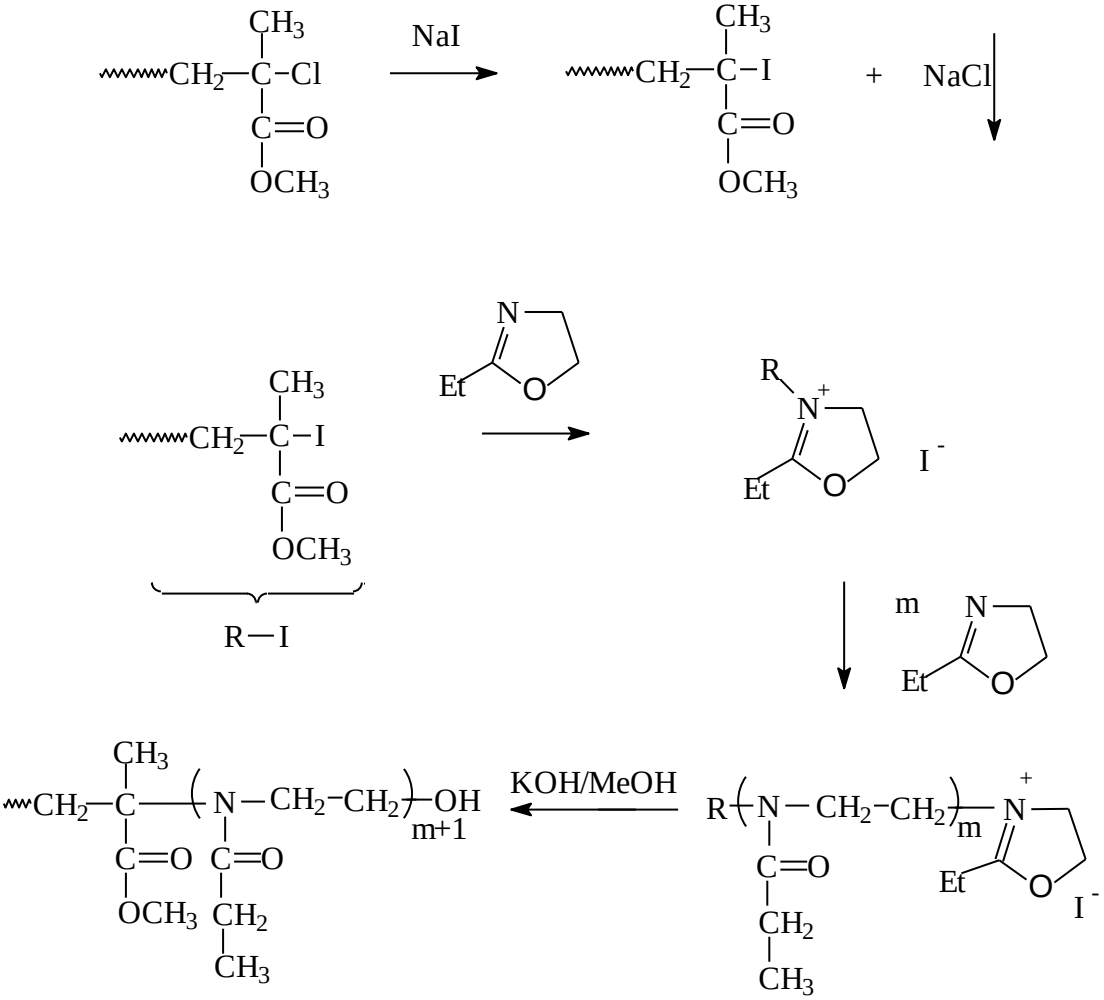


Scheme 4.2 Atom Transfer Radical Polymerization (ATRP) of PMMA and PSt as a schematic representation

For the polymerization of MMA; CuCl, complexed by PMDETA, was used as the catalyst at 90^{o}C in 50 vol. % diphenylether. For the polymerization of PSt; CuBr, complexed by PMDETA, was used as the catalyst at 110^{o}C. Consequently PMMA macroinitiator with chlorine-ended , and PSt macroinitiators with bromine-ended were formed. The results are presented in Table 4.2 for PMMA, and in Table 4.3 and 4.4 for PSts.

4.3 The Synthesis of P(MMA-*b*-EtOZO) Block Copolymers by CROP

PMMA macroinitiator is used to polymerize 2-ethyl-2-oxazoline, affording poly (methyl methacrylate-*b*-2-ethyl-2-oxazoline) (P(MMA-*b*-EtOZO) block copolymers. Sodium iodide was used to convert the chloride functionality to the more reactive iodide. Synthesis of P(MMA-*b*-EtOZO) block copolymers by CROP is shown in scheme 4.3. The results for P(MMA-*b*-EtOZO) block copolymers are summerized in table 4.2.



Scheme 4.3 Synthesis of P(MMA-*b*-EtOZO) block copolymers by CROP

Table 4.2 Synthesis of PMMA macroinitiator and P(MMA-*b*-EtOZO) block copolymers

Run	Monomer	Init.	Time (h)	Conv. (%)	Mn_{theo} [d]	Mn_{GPC} [e]	M_w/M_n	Mn_{Hnmr} [f]	Composition ^{1}H NMR
P-IV[a]	MMA	EIBR	1/3	35	3500	3700	1,17	-	-
P-V[b]	EtOZO	P-IV	3.5	22	5400	2700	1,75	32600	%11 PMMA, %89 PEtOZO
P-VI[c]	EtOZO	P-IV	5	32	6200	5200	1,82	25000	%15 PMMA, %85 PEtOZO

EIBR: Ethyl 2-bromo-isobutyrate

[a] $[M]_0 : [I]_0 : [PMDETA]_0:[CuCl]_0=100:1:1:1$, the polymerization was carried out at 90°C in diphenyl ether (DPE), (MMA/DPE=2, v/v), $[M]_0$mol l^{-1} = 18,66

[b] $[M]_0 : [I]_0 : [NaI] = 80 : 1 : 2$, $[NaI]=2[I]_0$,the polymerization was carried out at 110°C in bulk.

[c] $[M]_0 : [I]_0 : [NaI] = 80 : 1 : 2$, $[NaI]=2[I]_0$,the polymerization was carried out at 110°C in acetonitrile (AN), (EtOZO/AN=1, v/v), $[M]_0$mol l^{-1} = 9,9

[d] $M_{n\ (theoretical)} = ([M_o]/[I_o]) * (\%\ Conversion/100) * MW_{monomer} + MW_{\ macroinitiator}$

[e] Molecular weight of the macroinitiator and block copolymers was calculated with the aid of poly (methyl methacrylate) and polystyrene standarts, respectively.

[f] By integrating the signals of $–NCH_2CH_2$ protons of 2-ethyl-2-oxazoline, 3.43 ppm, and $-OCH_3$ protons of methyl methacrylate, 3.58ppm, the compositions of block copolymers were determined.

GPC traces of PMMA macroinitiator (P-IV) and P(MMA-*b*-EtOZO) block copolymer (P-VI) are presented in Figure 4.2 . The peak corresponding to diblock copolymer clearly schifted to higher molecular weight region of the chromotogram.

As a result of the formed PEtOZO homopolymer which is observed in GPC trace of P(MMA-*b*-EtOZO) block copolymer (P-VI) in figure 4.2, the experimentally obtained molecular weights (Mn_{GPC} and Mn_{NMR}) are not in agreement with each other. Also molecular weights determined by ^{1}H NMR spectroscopy are higher than the theoretical molecular weights for all cases indicating low initiator efficiency.

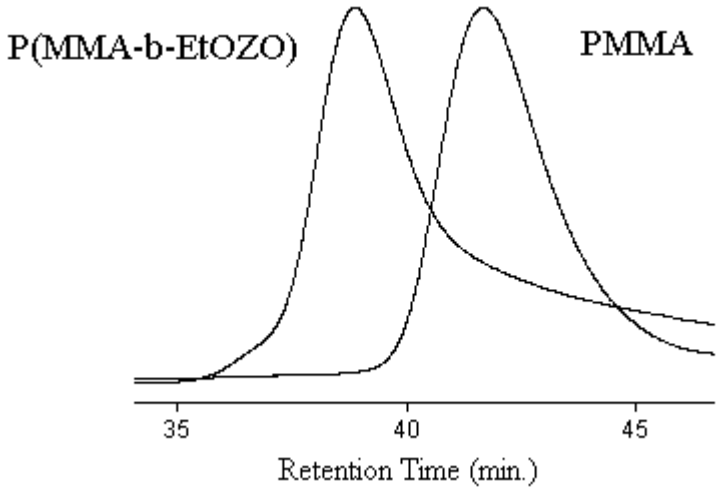


Figure 4.2 GPC traces of PMMA macroinitiator (P-IV) and P(MMA-*b*-EtOZO) block copolymer (P-VI)

^{1}H-NMR spectrum of P(MMA-*b*-EtOZO) block copolymer (P-VI) is seen in figure 4.3. The composition and molecular weight of diblock copolymers were determined via ^{1}HNMR measurements. ^{1}HNMR spectra of all P(MMA-*b*-EtOZO) diblock copolymers exhibit major peaks that are characteristics of the PMMA and PEtOZO segments.

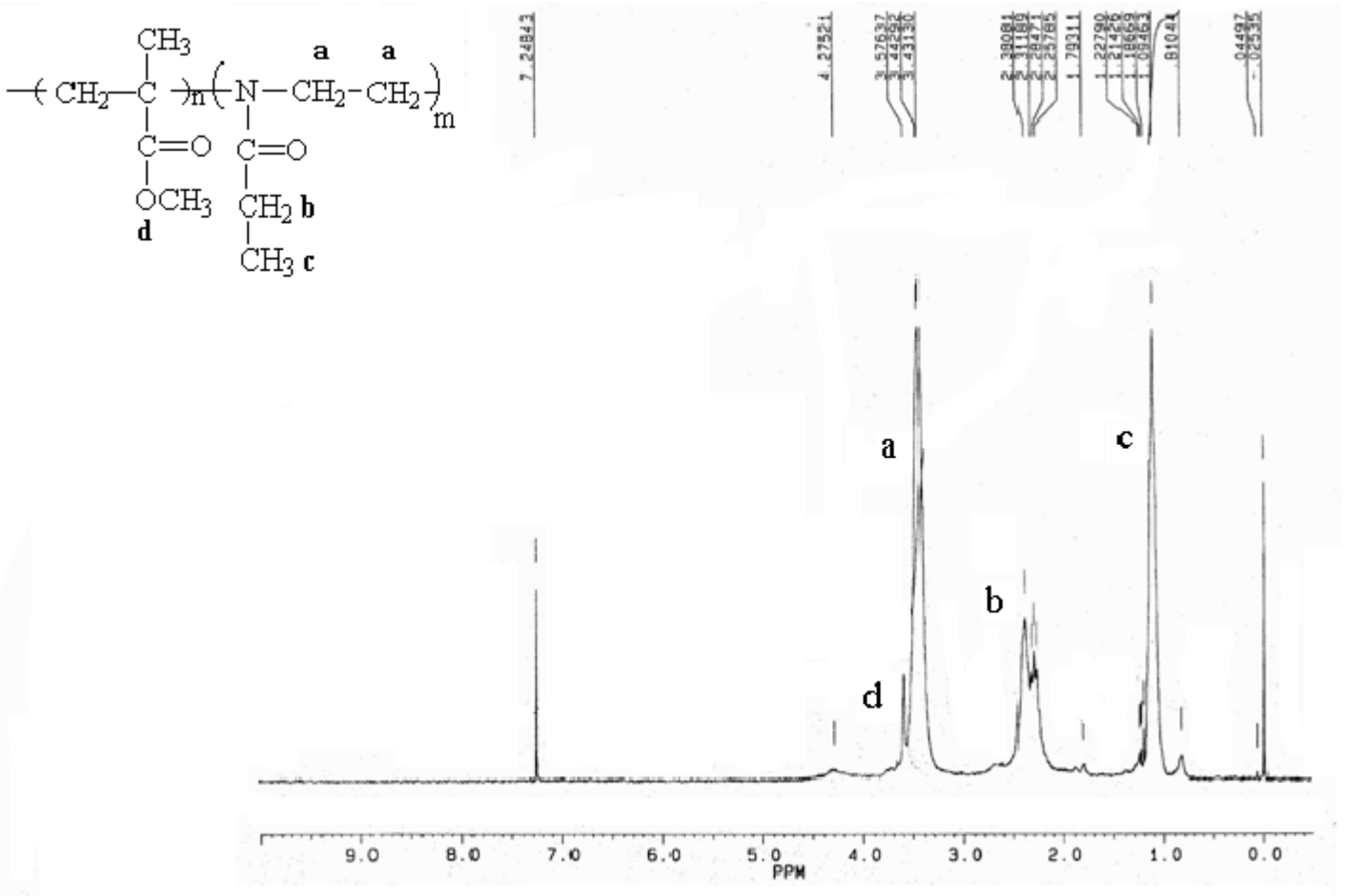
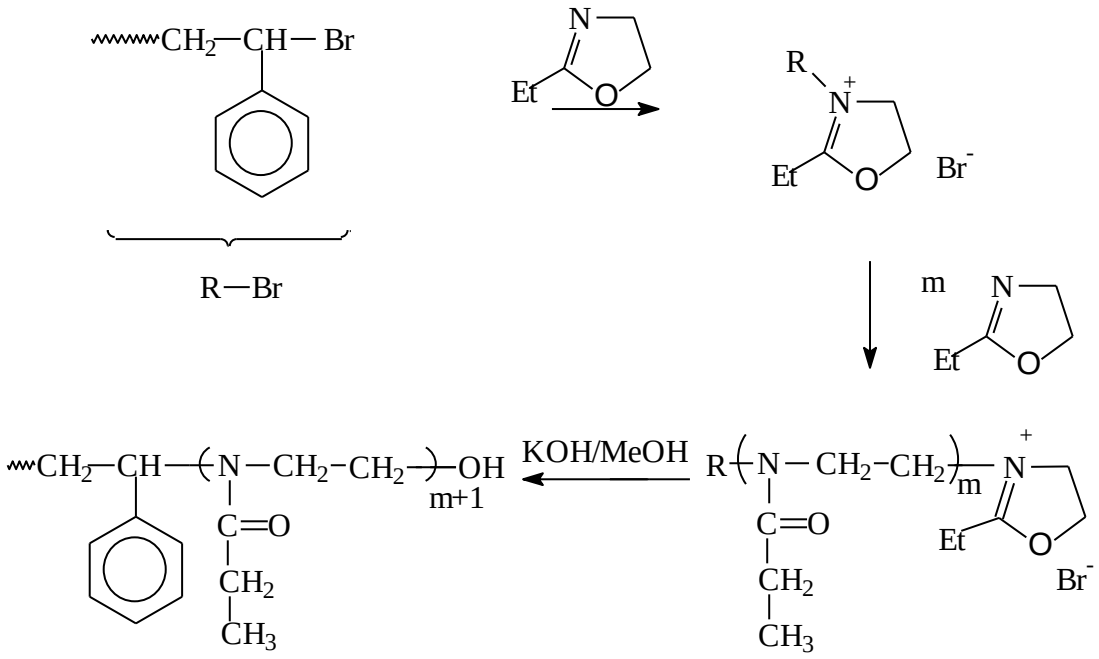


Figure 4.3 ^{1}H NMR spectrum of P(MMA-*b*-EtOZO) block copolymer (P-VI)

4.4 The Synthesis of P(St-*b*-EtOZO) Block Copolymers by CROP

Bromine-ended PSt macroinitiators are used to initiate the cationic ring opening polymerization of 2-ethyl-2-oxazolines. Diblock copolymers consisting of St and EtOZO segments are obtained. The polymerization is conducted at 110^{o}C. Synthesis of P(St-*b*-EtOZO) block copolymers is shown in scheme 4.4. The results are given in table 4.3. and 4.4



Scheme 4.4 Synthesis of P(St-*b*-EtOZO) block copolymers

Table 4.3 Synthesis of PSt macroinitiator and P(St-*b*-EtOZO) block copolymers

Run	Monomer	Init.	Time (h)	Conv. (%)	Mn_{theo} [e]	Mn_{GPC} [f]	M_w/M_n	Mn_{Hnmr} [g]	Composition ^{1}H NMR
P-VII[a]	St	BPE	1/4	24	2500	2300	1.12	-	-
P-VIII[b]	EtOZO	P-VII	17	81	8700	7500	1,53	20000	%11 PSt, %88 PetOZO
P-IX[c]	EtOZO	P-VII	17	95	9800	13500	2,1	24000	%9 PSt, %91 PetOZO
P-X[d]	-	-	-	-	9800	23000	1,32	26000	%8 PSt, %92 PetOZO

BPE : 1-bromo-1-phenyl ethane

[a] $[M]_0 : [I]_0 : [PMDETA]_0 : [CuCl]_0 = 100 : 1 : 1 : 1$, the polymerization was carried out at 110^0C in bulk.

[b] $[M]_0 : [I]_0 = 80 : 1$,the polymerization was carried out at 110^0C in acetonitrile(AN), (EtOZO/AN= 1, v/v), $[M]_0$mol $l^{-1} = 9,9$

[c] $[M]_0 : [I]_0 = 80 : 1$,the polymerization was carried out at 110^0C in bulk.

[d] After selective extraction of block copolymer (P-IX).

[e] Theoretical molecular weights were calculated by the formula;
$M_{n\,(theoretical)} = ([M_o]/[I_o]) \times (\text{Conversion \%}) \times MW_{monomer} + MW_{macroinitiator}$

[f] Molecular weight of the polymers was calculated with the aid of polystyrene standarts.

[g] By integrating the signals of $-NCH_2CH_2$ protons of 2-ethyl-2-oxazoline, 3.43 ppm, and aromatic protons of styrene, between 6.5 and 7.0 ppm, compositions of diblock copolymers were determined.

Table 4.4 Synthesis of PSt macroinitiator and P(St-*b*-EtOZO) block copolymers

Run	Monomer	Init.	Time (h.)	Conv. (%)	Mn_{theo} [e]	Mn_{GPC} [f]	M_w/M_n	Mn_{Hnmr} [g]	Composition ^{1}H NMR
P-XI[a]	St	BPE	1/3	33	3400	3400	1,11	-	-
P-XII[b]	EtOZO	P-X	16	75	12300	9800	1,81	175000	%2 PSt, %98 PEtOZO
P-XIII[c]	EtOZO	P-X	18	96	13000	8900	2,02	111000	%3 PSt, %97 PEtOZO
P-XIV[d]	EtOZO	P-X	23	88	13900	12300	1,52	43000	%8 PSt, %92 PEtOZO

[a] $[M]_0 : [I]_0 : [PMDETA]_0 : [CuCl]_0 = 100 : 1 : 1 : 1$, the polymerization was carried out at 110^0C in bulk.

[b] $[M]_0 : [I]_0 = 120 : 1$, the polymerization was carried out at 110^0C in acetonitrile(AN), (EtOZO/AN= 1, v/v), $[M]_0$mol l^{-1} =9,9

[c] $[M]_0 : [I]_0 = 100 : 1$, the polymerization was carried out at 110^0C in acetonitrile(AN), (EtOZO/AN= 1, v/v), $[M]_0$mol l^{-1} = 9,9

[d] $[M]_0 : [I]_0 = 120 : 1$, the polymerization was carried out at 110^0C in acetonitrile(AN), (EtOZO/AN= 1/2, v/v), $[M]_0$mol l^{-1} = 4.95

[e] Theoretical molecular weights were calculated by the formula;
$M_{n\,(theoretical)} = ([M_o]/[I_o]) \times (\text{Conversion \%}) \times MW_{monomer} + MW_{macroinitiator}$

[f] Molecular weight of the polymers was calculated with the aid of polystyrene standarts.

[g] By integrating the signals of $-NCH_2CH_2$ protons of 2-ethyl-2-oxazoline, 3.43 ppm, and aromatic protons of styrene, between 6.5 and 7.0 ppm, compositions of diblock copolymers were determined.

The GPC traces of macroinitiator PSt (P-VII) and block copolymer (P-IX) is seen in Figure 4.4 . Figure 4.5 shows the GPC traces after selective extraction (P-X). Figure 4.6 shows the GPC traces of PSt macroinitiator (P-VII) and P(St-*b*-EtOZO) block copolymer (P-VIII).

As can be seen from table 4.3 and 4.4 the experimentally obtained molecular weights (Mn_{GPC} and Mn_{NMR}) are not in agreement with each other as a result of the formation of PEtOZO homopolymer which was observed in the GPC traces of block copolymers (Fig 4.4 and fig 4.6).

In order to remove PEtOZO homopolymer, P(St-*b*-EtOZO) block copolymer (P-IX) was selectively extracted by using suitable solvents. First the obtained polymer was treated with water, by this way PEtOZO homopolymer which dissolves in water, was removed. Undissolved polymer was filtered and dissolved in THF. By the aid of a dessicant(Na_2SO_4) water is removed. Then excess THF was evaporated and the polymer was precipitated in diethyl ether. After filtration it was dried under vacuum at 50^oC. As seen in table 4.3 (P-X) after extraction experimentally obtained molecular weights (Mn_{GPC} and Mn_{NMR}) became in agreement with each other but they were higher than theoretical molecular weight. This indicates that the initiator efficiency of macroinitiator is low.

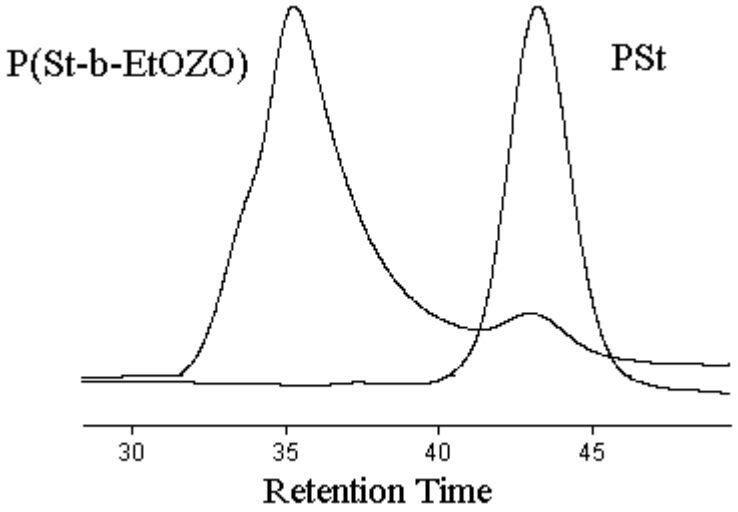


Figure 4.4 GPC traces of PSt macroinitiator (P-VII) and P(St-*b*-EtOZO) block copolymer (P-IX)

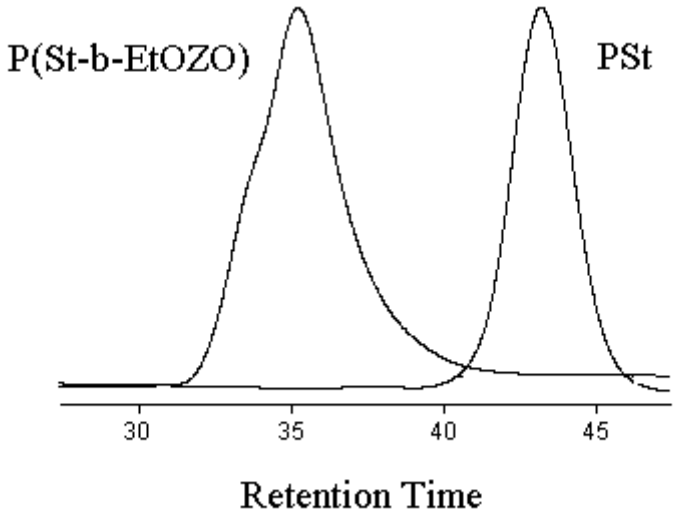


Figure 4.5 GPC traces of macroinitiator PSt (P-VII) and P(St-*b*-EtOZO) block copolymer (P-X)

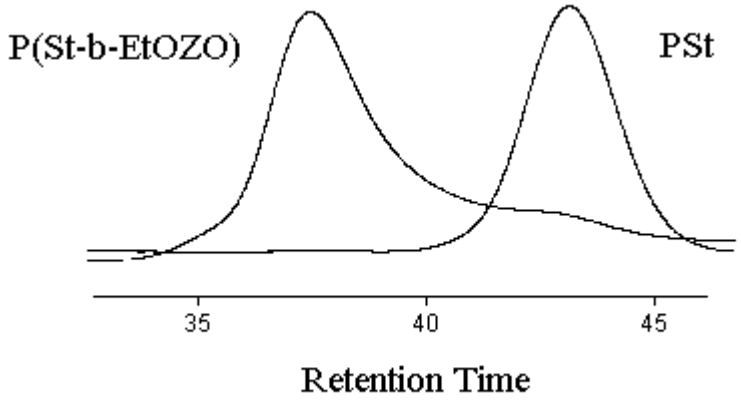


Figure 4.6 GPC traces of PSt macroinitiator (P-VII) and P(St-*b*-EtOZO) block copolymer (P-VIII)

^{1}H-NMR spectrum of P(St-*b*-EtOZO) block copolymer (P-VIII) is seen in figure 4.7. The composition and molecular weight of diblock copolymers were determined via ^{1}HNMR measurements. ^{1}HNMR spectra of all P(St-*b*-EtOZO) diblock copolymers exhibit major peaks that are characteristics of the PSt and PEtOZO segments.

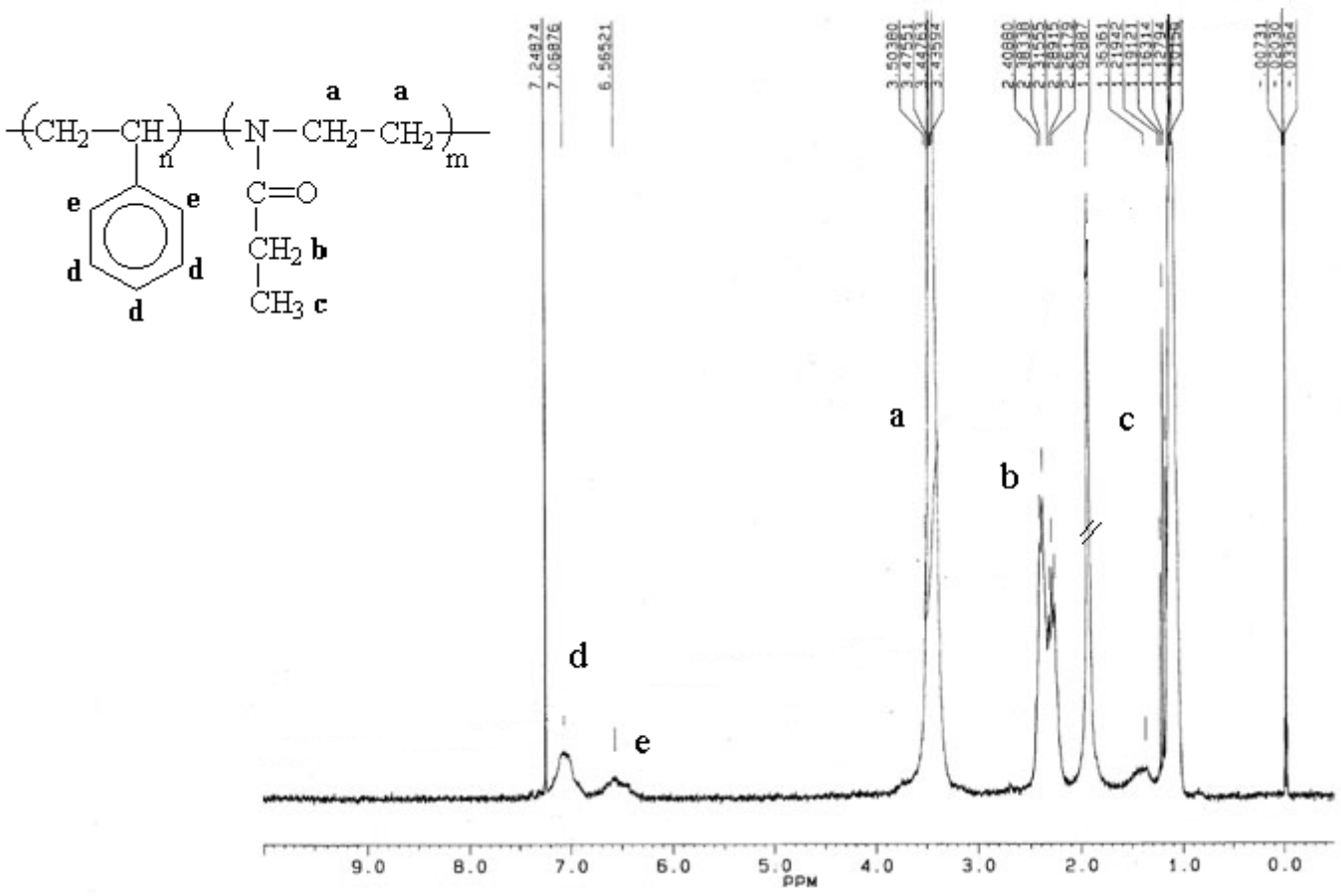


Figure 4.7 ^{1}H NMR spectrum of P(St-*b*-EtOZO) block copolymer (P-VIII)

5. CONCLUSION & RECOMENDATIONS

In conclusion, amphiphilic poly (methyl methacrylate-b-2-ethyl-2-oxazoline) P(MMA-b-PEtOZO) and poly (styrene-b-2-ethyl-2-oxazoline) P(St-b-PEtOZO) block copolymers were synthesised by using halogen-ended, well defined PMMA and PSt macroinitiators which were obtained by atom transfer radical polymerization (ATRP). Diblock copolymers were characterized by Gel Permeation Chromatography (GPC) and ^{1}HNMR spectroscopy. MMA polymerization was conducted at 90 ^{0}C in DPE using CuCl/PMDETA catalyst system where St polymerizations was carried out at 110 ^{0}C in bulk using CuBr/PMDETA catalyst system .

It was seen that, as a result of the formed PEtOZO homopolymer observed in the GPC traces of block copolymers, the experimental number average molecular weights, determined by GPC and ^{1}HNMR spectroscopy were not in agreement with each other. After selective extraction of the P(St-*b*-PEtOZO) block copolymers with a suitable solvent, like water, formed PEtOZO homopolymer is removed. Experimental molecular weights became compatible with each other, but they were higher than theoretical molecular weights, indicating low initiator efficiency.

In this study, we have demonstrated that halogen ended PMMA and PSt macroinitiators obtained via ATRP can initiate the cationic ring opening polymerization of 2-ethyl-2-oxazoline resulting in the formation of P(MMA-*b*-EtOZO) and P(St-*b*-EtOZO) block copolymers. Hydroxyl groups were introduced to the end of the PEtOZO chains of these block copolymers by treatment with methanolic KOH. In a further study the hydroxyl groups of block copolymers can be used as the initiation sites for the ring opening polymerization of ε-caprolactone monomer to produce PMMA-PEtOZO-PCL and PMMA-PEtOZO-PCL triblock copolymers.

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